

ELECTROCHEMICAL CELL SUITABLE FOR USE IN ELECTRONIC DEVICES

The present invention relates to a novel electrochemical cell, which may be a
5 battery or a supercapacitor or both, and which is suitable for use in portable and other electronic devices, and specifically to such a cell having at least the positive electrode formed of a mesoporous material having a periodic arrangement of substantially uniformly sized pores of cross-section of the order of 10^{-8} to 10^{-9} m.

It should be noted that the term "battery" is used herein in its common meaning
10 of a device that converts the chemical energy contained in its active components directly into electrical energy by means of a redox (oxidation-reduction) reaction. The basic unit of a battery is an electrochemical cell, which will comprise at least a positive electrode, a negative electrode and an electrolyte, the whole contained within a casing. Other components, such as separators, may be included, as is well known in the art. A
15 battery may consist of one or more such cells.

Many portable electronic devices require power to be available as a steady flow at a relatively low level, interspersed with spikes or surges of much higher power drain. Most conventional batteries are unable to meet these requirements and so may be supplemented with a capacitor or supercapacitor, which stores power when it is not
20 required by the device and releases it when required. Examples of devices having this type of power requirement include notebook computers, mobile telephones, PDAs (personal digital assistants – i.e. microcomputers), defibrillators and the like. However, in such portable devices a high premium is put on portability, which is a function of both weight and size. Any additional equipment in the device inevitably adds to both of
25 these, rendering the device less portable and so less desirable.

A consequent requirement of any electrochemical cell which is to function in such a portable device is that it should have both high power and high energy densities. In the past, it has only been possible to achieve one or the other of these at reasonable cost, and not both.

We have now discovered that the technology of mesoporous films, disclosed, for example, in EP 993 512 or US 6,203,925, may be applied to the production of one or both electrodes of an electrochemical cell, and that the resulting electrochemical cell, which may function as a battery, as a capacitor or as both, can be designed to have both
5 high power density and high energy density.

Thus, the present invention provides an electrochemical cell, which may, for example, be used in a portable electronic device, said cell having a positive electrode, a negative electrode and an electrolyte, characterised in that at least the positive electrode comprises a mesoporous structure having a periodic arrangement of substantially
10 uniformly sized pores of cross-section of the order of 10^{-8} to 10^{-9} m.

The invention also provides a portable electronic device containing such an electrochemical cell.

The invention still further provides an automotive battery comprising a plurality of the electrochemical cells of the present invention.

15 The electrochemical cell of the present invention may be constructed to function as a battery, as a supercapacitor or as a combined battery/supercapacitor. For example, a supercapacitor having mesoporous positive and negative electrodes operates via the mechanism of proton shuttling between a mesoporous positive electrode, e.g. of $\text{Ni}(\text{OH})_2$, and a hydrogen absorbing mesoporous negative electrode, e.g. of palladium,
20 as illustrated in the schematic of Figure 1. The mechanism is similar to that operating in Ni-MH batteries where the palladium is replaced by another hydrogen absorbing material such as LaNi_5 .

Examples of portable electronic devices which may include the electrochemical cell of the present invention include: portable computers, including the so-called
25 notebook computers, desktop replacement computers, ultraportable computers etc. (the present invention being of particular value in the smaller versions, such as the ultraportables); mobile telephones; cordless (landline) telephones; PDAs; portable hard disk drives; music players of various sorts, including CD players, cassette players, mini-disk players and other digitally recorded music players, including MP3 and like
30 software-based music players; portable televisions; portable DVD players; portable

radios; hybrid devices (i.e. devices serving two or more previously separate functions), such as PDA/mobile telephones, telephone/music players, hard disk storage/music players etc.; and medical devices, such as defibrillators.

The electrochemical cells of the present invention may also be used in
5 automotive batteries.

All of the above devices require a steady supply of power at a relatively low level, interspersed with periodic demands for much higher power at essentially random intervals. They are, therefore especially suited for use with the electrochemical cells of the present invention. The specifics of the design and construction of these devices is
10 well known and, beyond the incorporation of an electrochemical cell according to the present invention, does not form a part of the present invention.

At least the positive electrode, the cathode, of the electrochemical cell of the present invention is formed of a mesoporous material. The material is preferably a metal, a metal oxide, a metal hydroxide, a metal oxy-hydroxide or a combination of any
15 two or more of these. Examples of such metals include: nickel; alloys of nickel, including alloys with a transition metal, nickel/cobalt alloys and iron/nickel alloys; cobalt; platinum; palladium; and ruthenium. Examples of such oxides, hydroxides and oxy-hydroxides include: gold oxide; palladium oxide; nickel oxide (NiO); nickel hydroxide (Ni(OH)₂); nickel oxy-hydroxide (NiOOH); and ruthenium oxide. Of these,
20 we most prefer nickel and its oxides and hydroxides.

As is well known in the field, certain of these materials require "conditioning" before use. This may be achieved by putting the cell through several cycles of charging and discharging, as is conventional in the art. A typical material requiring such conditioning is nickel, which, as a result of the conditioning, will acquire a surface layer
25 of an oxide.

There is no limitation on the nature of the material used to manufacture the negative electrode, the anode, of the electrochemical cell of the present invention, and any material may be used having regard to the chemistry of the cell which is to be made. Examples of suitable materials include: carbon; cadmium; iron; a palladium/nickel
30 alloy; an iron/titanium alloy; palladium; or a mixed metal hydride, for example

LaNi₅H_X. These materials are preferably porous, and more preferably mesoporous. Of these, preferred materials are carbon and palladium. Mesoporous palladium is, however, not the preferred negative electrode material for low cost applications, due to its high cost.

5 Preferred combinations of anode and cathode are Nickel/Palladium, Nickel/Carbon, Nickel/Iron and Nickel/Cadmium, of which Nickel/Carbon is most preferred. Where reference is made to nickel, the oxides and hydroxides thereof are also included.

In particular, we prefer that the mesoporous structure of the positive electrode
10 comprises nickel and an oxide, hydroxide or oxy-hydroxide of nickel selected from NiO, Ni(OH)₂ and NiOOH, said nickel oxide or hydroxide forming a surface layer over said nickel and extending over at least the pore surfaces, and the negative electrode comprises nanoparticulate carbon.

Thus, preferably the positive electrode and the negative electrode each comprise
15 a mesoporous structure having a periodic arrangement of substantially uniformly sized pores of cross-section of the order of 10⁻⁸ to 10⁻⁹ m. The positive electrode, and the negative electrode if it also is mesoporous, consists of or consists substantially of the mesoporous structure or structures as defined.

By "mesoporous structure", "mesoporous material" and "mesoporous film" as
20 referred to herein are meant structures, materials and films, respectively, that have been fabricated via a liquid crystal templating process, and that consequently are monolithic in nature, and contain a long range, regular arrangement of pores having a defined topology and a substantially uniform pore size (diameter). Accordingly, the mesoporous structures, materials and films may also be described as nanostructured or
25 having nanoarchitecture.

Therefore, the mesoporous materials used in accordance with the invention are distinct from poorly crystallised materials and from composites with discrete nano-sized solid grains, e.g. conventionally denoted 'nanomaterials' that are composed of aggregated nanoparticulates.

An advantage of using mesoporous materials, compared with nanomaterials, is that electron transport within the mesoporous material does not encounter grain boundary resistances, affording superior electronic conductivity and removing power losses associated with this phenomenon. Moreover, the ordered porosity of the
5 mesoporous materials used here provides a continuous and relatively straight, non-tortuous path of flow with uniform diameter, encouraging the rapid and unhindered movement of electrolyte species. By contrast, conventional nanoparticulate systems have a disordered porosity with voids of varying cross section interconnected by narrower intervoid spaces. As such, substances moving within the pore structure
10 encounter a considerably tortuous path, impeding reaction rates.

The mesoporous material is preferably in the form of a film of substantially constant thickness. Preferably, the mesoporous film thickness is in the range from 0.5 to 5 micrometers.

Preferably, the mesoporous material has a pore diameter within the range from
15 about 1 to 10 nanometres, more preferably within the range from 2.0 to 8.0 nm.

The mesoporous material may exhibit pore number densities in the range from 1×10^{10} to 1×10^{14} pores per cm^2 , preferably from 4×10^{11} to 3×10^{13} pores per cm^2 , and more preferably from 1×10^{12} to 1×10^{13} pores per cm^2 .

The mesoporous material has pores of substantially uniform size. By
20 "substantially uniform" is meant that at least 75%, for example 80% to 95%, of pores have pore diameters to within 30%, preferably within 10%, and most preferably within 5%, of average pore diameter. More preferably, at least 85%, for example 90% to 95%, of pores have pore diameters to within 30%, preferably within 10%, and most preferably within 5%, of average pore diameter.

25 The pores are preferably cylindrical in cross-section, and preferably are present or extend throughout the mesoporous material.

The mesoporous structure has a periodic arrangement of pores having a defined, recognisable topology or architecture, for example cubic, lamellar, oblique, centred rectangular, body-centred orthorhombic, body-centred tetragonal, rhombohedral,

hexagonal. Preferably, the mesoporous structure has a periodic pore arrangement that is hexagonal, in which the electrode is perforated by a hexagonally oriented array of pores that are of uniform diameter and continuous through the thickness of the electrode.

In the preferred case where the pore arrangement is hexagonal, the arrangement
5 of pores has a regular pore periodicity, corresponding to the centre-to-centre pore
spacing, preferably in the range from 3 to 15 nm, more preferably in the range from 5 to
9 nm.

Moreover, the mesoporous structure having this regular periodicity and
substantially uniform pore size should extend over a portion of the electrode of the
10 order of at least 10 times, preferably at least 100 times, the average pore size.
Preferably, the electrode consists of or consists substantially of a structure or structures
as defined.

It will be appreciated that these pore topologies are not restricted to ideal
mathematical topologies, but may include distortions or other modifications of these
15 topologies, provided recognisable architecture or topological order is present in the
spatial arrangement of the pores in the film. Thus, term "hexagonal" as used herein
encompasses not only materials that exhibit mathematically perfect hexagonal
symmetry within the limits of experimental measurement, but also those with
significant observable deviations from the ideal state, provided that most channels are
20 surrounded by an average of six nearest-neighbour channels at substantially the same
distance. Similarly, the term "cubic" as used herein encompasses not only materials that
exhibit mathematically perfect symmetry belonging to cubic space groups within the
limits of experimental measurement, but also those with significant observable
deviations from the ideal state, provided that most channels are connected to between
25 two and six other channels.

The electrolyte in the cell is preferably an aqueous electrolyte, for example an
aqueous alkaline electrolyte such as aqueous potassium hydroxide.

In a preferred embodiment, the mesoporous structure of the positive electrode
comprises nickel and an oxide, hydroxide or oxy-hydroxide of nickel selected from
30 NiO, Ni(OH)₂ and NiOOH, said nickel oxide, hydroxide or oxy-hydroxide forming a

- surface layer over said nickel and extending over at least the pore surfaces, and the negative electrode has a mesoporous structure of carbon or palladium. When filled with electrolyte, the positive electrode represents a three-phase composite composed of an interconnected Ni current collector base, coated with Ni(OH)_2 active material which is
- 5 in contact with the electrolyte. Advantageously, the hydrous structure of the mesoporous Ni positive electrode is retained such that both surface and bulk processes can contribute to the charge capacity of the electrode. Due to the nanoscale structure of the electrode, all three phases are in either in intimate contact or within about 1-2 nm of each other and the overall surface area of the 'phase boundaries' is extremely high.
- 10 Hence, a high energy density can be achieved, whilst the small proton diffusion distance enables the cell to exhibit very high power density.

The mesoporous materials used as the positive, and optionally the negative, electrodes of the electrochemical cells of the present invention are prepared by a liquid crystal templating method, and preferably are deposited as films on a substrate by

15 electrochemical deposition from a lyotropic liquid crystalline phase. They may also be prepared by electro-less deposition, such as by chemical reduction from a lyotropic liquid crystalline phase.

Suitable substrates include gold, copper, silver, aluminium, nickel, rhodium or cobalt, or an alloy containing any of these metals, or phosphorus. The substrate may, if

20 desired, be microporous, with pores of a size preferably in the range from 1 to 20 micrometres. The substrate preferably has a thickness in the range from 2 to 50 micrometres. The substrate preferably is a substrate as above, other than gold, having a layer of gold formed on it by vapour deposition.

Suitable methods for depositing mesoporous materials as films onto a substrate

25 by electrochemical deposition and chemical means are known in the art. For example, suitable electrochemical deposition methods are disclosed in EP-A-993,512; Nelson, et al., "*Mesoporous Nickel/Nickel Oxide Electrodes for High Power Applications*", J. New Mat. Electrochem. Systems, 5, 63-65 (2002); Nelson, et al., "*Mesoporous Nickel/Nickel Oxide – a Nanoarchitected Electrode*", Chem. Mater., 2002, 14, 524-

30 529. Suitable chemical reduction methods are disclosed in US-A-6,203,925.

Preferably, the mesoporous material is formed by electrochemical deposition from a lyotropic liquid crystalline phase. According to a general method, a template is formed by self-assembly from certain long-chain surfactants and water into a desired liquid crystal phase, such as a hexagonal phase. Suitable surfactants include

- 5 octaethylene glycol monohexadecyl ether ($C_{16}EO_8$), which has a long hydrophobic hydrocarbon tail attached to a hydrophilic oligoether head group. Others include the polydisperse surfactants Brij[®] 56 ($C_{16}EO_n$ where n~10), Brij[®] 78 ($C_{16}EO_n$ where n~20), and Pluronic 123, each available from Aldrich. At high (>30%) aqueous concentrations, and dependent on the concentration and temperature used, the aqueous
10 solution can be stabilised in a desired lyotropic liquid crystal phase, for example a hexagonal phase, consisting of separate hydrophilic and hydrophobic domains, with the aqueous solution being confined to the hydrophilic domain. Dissolved inorganic salts, for example nickel acetate, will also be confined to the hydrophilic domain, and may be electro-reduced at an electrode immersed in the solution, to form a solid mesophase, for
15 example of nickel metal, that is a direct cast of the aqueous domain phase structure. Subsequent removal of the surfactant, by washing in a suitable solvent, leaves a regular periodic array of pores in the electro-reduced solid, the arrangement of the pores being determined by the lyotropic liquid crystal phase selected. The topology, size,
periodicity and other pore characteristics may be varied by appropriate selection of the
20 surfactant, solvent, metal salts, hydrophobic additives, concentrations, temperature, and deposition conditions, as is known in the art.

- As noted above, the mesoporous material of which the mesoporous electrode is made is preferably formed by electrodeposition or chemical deposition on a substrate. Since the mesoporous material may lack adequate mechanical strength, it is preferably
25 used as an electrode on a substrate, and, for convenience, this is preferably the same substrate as was used in its preparation.

The invention is further illustrated by the following non-limiting examples, with reference to the Figures, in which:

- Figure 1 represents a schematic drawing showing the flow of protons on charge
30 and discharge to and from a Pd lattice into a NiOOH positive electrode proton sink;

Figure 2 shows a comparison of the cyclic voltammetry of a 1 mm diameter H_I Pd disc (—) with that of a 200 μm H_I Ni disc (---) in 6 M KOH at 20 mV s⁻¹;

Figure 3 shows the charge/discharge behaviour of a 200 μm H_I Ni disc based supercapacitor by cyclic voltammetry at 20 mV s⁻¹ separated by 1 cm in 6 M KOH;

5 Figure 4 shows the flow of charge from the device versus potential during the 20 mV s⁻¹ discharge depicted in Figure 3;

Figure 5 shows the potential step charging/discharging of a H_I Ni/H_I Pd supercapacitor in 6 M KOH composed of a 200 μm H_I Ni disc with a 1 cm² H_I Pd electrode in 6 M KOH;

10 Figure 6 shows a comparison of the first full cycle (—) of a 1 cm² H_I Ni/1 cm² H_I Pd supercapacitor incorporating a porous PTFE separator with the 15000th cycle (---) at 500 mV s⁻¹;

15 Figure 7 represents a schematic drawing of the H_I electrode structure showing a pore ringed by oxidised active material Ni(OH)₂ which is held in a matrix of a nickel current collector, and further showing the active material occupying 45 % of the electrode bulk area;

Figure 8 shows a cyclic voltammogram of nanostructured nickel/nickel hydroxide electrode, as prepared in Example 10;

20 Figure 9 shows a cyclic voltammogram of high surface area carbon electrode, as prepared in Example 10;

Figure 10 shows a cyclic voltammogram of nickel-carbon supercapacitor, as prepared in Example 10;

Figure 11 shows the potential-charge relationship of the cyclic voltammogram of nickel-carbon supercapacitor of Figure 10; and

25 Figure 12 shows the potential step of the nickel-carbon supercapacitor of Figure 10 (8 cm², 93.7 mg) pulsed between 0 V and 1.4 V in 6 M KOH at 25 °C;

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Figure 13 shows a cyclic voltammogram of a liquid crystal templated iron electrode between -0.3 V and -1.2 V vs. Hg/HgO in 6 M KOH at 20 mV s⁻¹ and 25 °C, as prepared in Example 11;

5 Figure 14 shows the potential-charge relationship of the cyclic voltammogram shown in Figure 13;

Figure 15 shows a cyclic voltammogram of mesoporous nickel versus liquid crystal templated iron in a two electrode set-up between 0 V and 1.4 V in 6 M KOH at 5 mV s⁻¹ and 25 °C, as prepared in Example 11; and

10 Figure 16 shows the potential-charge relationship of the cyclic voltammogram shown in Figure 15.

The invention is further illustrated by the following non-limiting Examples.

EXAMPLE 1

Electrodeposition of platinum from an hexagonal liquid crystalline phase:

3 grams of octaethylene glycol monohexadecyl ether (C₁₆EO₈) surfactant were added to 2.0 grams of water and 2.0 grams of hexachloroplatinic acid hydrate in water. The mixture was heated and shaken vigorously until a homogeneous mixture was obtained. Electrodeposition from this mixture was carried out at temperatures between 25°C and 85°C onto a 0.000314 centimetre squared polished gold electrode by stepping the potential from +0.6 volt vs. standard calomel electrode to -0.1 volt vs. standard 15 calomel electrode until a reduction charge of 2 millicoulomb was passed. The surfactant was removed by rinsing with distilled water. A film having a metallic structure was obtained, which upon examination by transmission electron microscopy obtained, which upon examination by transmission electron microscopy was found to have an hexagonal disposition of pores with internal diameters of 25 Å (±1.5 Å) separated by metal walls of 25 Å (±2 Å) width.

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EXAMPLE 2**Electrodeposition of platinum from an hexagonal liquid crystalline phase:**

The process of Example 1 was carried out using the shorter-chain surfactant C₁₂EO₈ in place of C₁₆EO₈. The pore diameters as determined by TEM were found to 5 be 17.5Å (±2Å).

EXAMPLE 3**Electrodeposition of platinum from an hexagonal liquid crystalline phase:**

The process of Example 1 was repeated using a quaternary mixture containing C₁₆EO₈ and n-heptane in the molar ratio 2:1. As determined by TEM, the pore 10 diameters were found to be 35Å (±1.5Å).

EXAMPLE 4**Electrodeposition of platinum from a cubic liquid crystalline phase:**

A mixture having normal topology cubic phase (indexing to the Ia3d space group) was prepared from 27 wt% of an aqueous solution of hexachloroplatinic acid 15 (33 wt% with respect to water) and 73 wt% of octaethylene glycol monohexadecyl ether (C₁₆EO₈). Electrodeposition onto polished gold electrodes was carried out potentiostatically at temperatures between 35°C and 42°C using a platinum gauze counterelectrode. The cell potential difference was stepped from +0.6 V versus the standard calomel electrode to -0.1 V versus the standard calomel electrode until a 20 charge of 0.8 millicoulombs was passed. After deposition the films were rinsed with copious amounts of deionised water to remove the surfactant. The washed nanostructured deposits were uniform and shiny in appearance. Transmission electron microscopy studies revealed a highly porous structure consisting of a three-dimensional periodic network of cylindrical holes with internal diameters of 25Å.

EXAMPLE 5**Electrodeposition of nickel from an hexagonal liquid crystalline phase:**

A mixture having normal topology hexagonal phase was prepared from 50 wt% of an aqueous solution of 0.2 M nickel (II) sulphate, 0.58 M boric acid, and 50 wt% of 5 octaethylene glycol monohexadecyl ether ($C_{16}EO_8$). Electrodeposition onto polished gold electrodes was carried out potentiostatically at 25°C using a platinum gauze counterelectrode. The cell potential difference was stepped to -1.0 V versus the saturated calomel electrode until a charge of 1 coulomb per centimetre squared was passed. After deposition the films were rinsed with copious amounts of deionised water 10 to remove the surfactant. The washed nanostructured deposits were uniform and shiny in appearance. Small angle X-ray diffraction studies of the electrodeposited tin revealed a lattice periodicity of 58Å, while transmission electron microscopy studies revealed a highly porous structure consisting of cylindrical holes with internal diameters of 34Å separated by nickel walls 28Å thick.

EXAMPLE 6

Depositions were carried out on gold plate electrodes at 25°C at a deposition potential of -0.1V vs. SCE (stepped from +0.6 V) from an hexagonal liquid crystalline phase consisting of 2.0g H_2O , 3.0g $C_{16}EO_8$ and 2.0g hexachloroplatinic acid. Thickness data were obtained by inspection of fractured samples using scanning electron 20 microscopy. The results are shown in Table 1 below:

Charge density (C cm ⁻²)	Film Thickness (nm)
0.64	92
1.0	277
2.0	517
4.00	744
6.37	1849
21.98	15455

Table 1. Relationship between charge density and nanostructured platinum film thickness.

EXAMPLE 7

Nanostructured platinum films were deposited from an hexagonal liquid crystalline phase consisting of 2.0g H₂O, 3.0g C₁₆EO₈ and 2.0g hexachloroplatinic acid. Depositions were carried out on 0.2 mm diameter gold disc electrodes at a deposition.

- 5 potential of -0.1 V vs. SCE (stepped from +0.6 V). The charge passed was 6.37 C cm⁻². Data were obtained from cyclic voltammetry in 2M sulphuric acid between potential limits -0.2 V and +1.2 V vs. SCE. The Roughness Factor is defined as the surface area determined from electrochemical experiments divided by the geometric surface area of the electrode. The results are shown in Table 2 below:

Temperature (°C)	Roughness Factor	Capacitance (μF cm ⁻²)
25	305	25510
35	379	29936
40	457	37580
50	517	40127
65	540	45541
75	581	55733
85	711	63376

10 Table 2. Effect of temperature on Roughness Factor and double layer capacitance.

EXAMPLE 8

Nanostructured platinum films were deposited from an hexagonal liquid crystalline phase consisting of 2.0g H₂O, 3.0g C₁₆EO₈ and 2.0g hexachloroplatinic acid. Depositions were carried out on 0.2 mm diameter gold disc electrodes at a deposition

- 15 potential indicated (stepped from +0.6 V). The charge passed was 6.37 C cm⁻². Data were obtained from cyclic voltammetry in 2M sulphuric acid between potential limits -0.2 V and +1.2 V vs. SCE. The results are shown in Table 3 below:

E_2 (V (vs. SCE))	Roughness Factor	Capacitance ($\mu\text{F cm}^{-2}$)
+0.1	34	4086
0.0	86	9268
-0.1	261	26105
-0.2	638	66783
-0.3	35	3924
-0.4	24	2250

Table 3. Effect of deposition potential on Roughness Factor and double layer capacitance.

Discussion of Examples 1 to 8:

5 The data in Examples 1 to 3 show how pore diameter can be controlled by variation of the chain length of the surfactant or by further addition of a hydrophobic hydrocarbon additive. Specifically, a comparison of Example 1 with Example 2 demonstrates that the pore size may be decreased by using a shorter-chain surfactant, whereas comparison of Example 1 with Example 3 shows that the pore size may be
10 increased by the addition of a hydrocarbon additive to the deposition mixture.

Example 6 demonstrates how the thickness of the deposited film may be controlled by varying the charge passed during electrodeposition.

Examples 7 and 8 show how the temperature and applied potential during electrodeposition affect the surface area and the double layer capacitance of the film.
15 As indicated by the Roughness Factor values, increasing the deposition temperature increases both the surface area and the double layer capacitance of the film. At the same time, the deposition potential may be so selected as to control the surface area and capacitance of the deposited film.

EXAMPLE 9**Preparation of mesoporous nickel and mesoporous palladium electrodes:****(i) Preparation of gold substrate:**

Gold discs (200 µm or 1 mm diameter) encased in an epoxy insulator, and thin film gold electrodes (approximately 1 cm²) made by evaporation of gold onto chromium-coated glass microscope slides, were prepared as follows, for subsequent deposition of mesoporous nickel and palladium electrodes:

The gold disc electrodes were cleaned by first polishing consecutively on 25 µm, 1 µm and 0.3 µm alumina (obtained from Buehler) embedded microcloths then cycling the electrodes between -0.6 V and 1.4 V vs. a saturated mercury sulphate reference electrode (SMSE) at 200 mVs⁻¹ for 5 min. in 2 M H₂SO₄ solution. With each cycle, a monolayer of gold oxide was formed and subsequently removed from the electrode surface.

The evaporated gold electrodes were cleaned in an ultrasonic bath of isopropanol for 60 minutes prior to deposition, then rinsed with de-ionized water and dried under ambient conditions.

(ii) Electrodeposition of nickel from an hexagonal liquid crystalline phase:

A mixture having normal topology hexagonal (H_I) phase was prepared from 35 wt% of an aqueous solution of 0.2 M nickel (II) acetate, 0.5 M sodium acetate and 0.2 M boric acid, and 65 wt% of Brij® 56 nonionic surfactant (C₁₆EO_n wherein n~10, from Aldrich), and electrodeposition onto polished gold substrate was carried out potentiostatically at 25°C using a platinum gauze counterelectrode, according to the method disclosed in Nelson et al., Chem. Mater., 2002, 14, 524-529. After deposition the films were washed in copious amounts of isopropanol for 24 hrs to remove the surfactant. A mesoporous nickel film of approximately 1 micrometer thickness and having an hexagonal arrangement of pores was obtained.

(iii) Electrodeposition of palladium from an hexagonal liquid crystalline phase:

A mixture having normal topology hexagonal (H_I) phase was prepared from 35 wt% of an aqueous solution of 0.5 M ammonium tetrachloropalladate (Premion, from Alfa Aesar), and 65 wt% of Brij[®] 56 nonionic surfactant ($C_{16}EO_n$ wherein n~10, from Aldrich). The presence of the H_I liquid crystalline phase in the palladium deposition template solution at 25 °C was confirmed using polarising light microscopy. Electrodeposition onto polished gold substrate was carried out potentiostatically at 25°C using a platinum gauze counterelectrode, according to the electrodeposition method disclosed in Bartlett et al., Phys. Chem. Chem. Phys., 2002, 4, 3835-3842, using the modified templating solution above. After deposition the films were washed in copious amounts of isopropanol for 24 hrs to remove the surfactant. A mesoporous palladium film of approximately 1 micrometer thickness and having an hexagonal arrangement of pores was obtained.

(iv) Actuation of electrodeposited mesoporous Ni and Pd electrodes:

The deposited mesoporous electrodes, as prepared in (ii) and (iii) above, were individually actuated by cyclic voltammetry prior to assembly of the supercapacitor. This was done in a three electrode cell containing 6 M KOH solution. The cell consisted of a Pyrex water-jacketed cell connected to a Grant ZD thermostated water bath, mercury/mercury oxide (6 M KOH) reference electrode (Hg/HgO) and a large area Pt gauze counter electrode. All experiments were carried out at 25 °C and potentials in experiments involving a reference electrode are quoted against the Hg/HgO reference.

The efficiency of the mesoporous nickel deposition process was quantified by anodic stripping voltammetry. This involved scanning the potential of a mesoporous nickel working electrode between -0.45 V and 0.9 V vs. a saturated calomel reference electrode (SCE) in 0.2 M HCl solution at 1 mV s⁻¹. The counter electrode was Pt gauze. The charge associated with the anodic nickel dissolution peak and comparison of this charge with the deposition charge gave a deposition efficiency of 34 %.

Cyclic voltammetry and potential step experiments were done using a custom made potentiostat and ramp generator interfaced with a National Instruments data acquisition card and LabVIEW software.

In order to compare the electrochemical characteristics of mesoporous Ni and mesoporous Pd, the cyclic voltammograms of both of these electrodes in 6 M KOH are overlaid in Figure 2. The anodic peak for Ni at 0.38 V vs. Hg/HgO shows oxidation of Ni(OH)₂ to NiOOH via Reaction (1) with subsequent reduction back to Ni(OH)₂ represented by the cathodic peak commencing at 0.4 V. The latter peak represents the proton storage capacity of the electrode, that is, the reversible capacity of the electrode for proton storage. In Figure 2, this is 295 mC cm⁻².

The electrochemistry of H₁Pd in 6 M KOH is more diverse with anodic currents due to oxide formation at positive potentials and subsequent stripping of this oxide with the cathodic peak at -0.25 V. Adsorption of hydrogen adatoms onto the Pd surface by formation of the surface palladium hydride is indicated by the small cathodic peak at around -0.75 V followed by the more substantial hydrogen absorption into the Pd lattice indicated by the large current superimposed on the hydrogen evolution current at potentials below -1 V. On reversal of potential in the positive direction hydrogen begins to desorb from the Pd as represented by the large anodic peak commencing at -0.8 V and peaking at -0.36 V. Based on comparison of the voltammetry of mesoporous Ni and mesoporous Pd, it may be expected that a charge storage device using these 2 electrodes would have a discharge voltage of approximately 1.2 V since this is approximately the potential difference between the onset of H⁺ desorption from Pd (-0.8 V vs. Hg/HgO) and the intercalation of H⁺ into NiOOH (0.4 V vs. Hg/HgO). This discharge voltage is variable with the state of charge of the Pd which can vary between -0.8 V vs. Hg/HgO for a fully charged electrode to -0.3 V vs. Hg/HgO where the Pd is fully discharged of hydrogen at 20 mV s⁻¹.

(v) **Assembly and testing of charge/discharge characteristics of supercapacitor:**

In order to study the performance and limitations of mesoporous nickel in a supercapacitor configuration, a negative electrode with higher capacity and power capability was needed. For this purpose, liquid crystal templated mesoporous

palladium, as prepared in (iii) above, was used. The size of the mesoporous palladium electrode was made significantly larger than the mesoporous nickel electrode such that performance limitations would be due to limitations in the nickel electrode.

Accordingly, a two-electrode supercapacitor without a separator was assembled
5 using a 200 μm diameter mesoporous nickel positive electrode of approximately 1 μm thickness in conjunction with a 1 cm^2 mesoporous palladium electrode separated by 1 cm in 6 M KOH solution. The deposition charge in synthesis of the mesoporous nickel in this case, as prepared in (ii) above, was -1.13 mC , which corresponds to a mass of 0.117 μg when taking into account a deposition efficiency of 34 %.

10 Figure 3 shows the cyclic voltammogram of the two-electrode supercapacitor cycled in the potential range 0 V to 1.3 V. At approximately 1.22 V the device is charged, corresponding to the removal of protons from the Ni(OH)_2 and formation of NiOOH . Discharge occurs as protons from the Pd lattice move into the NiOOH structure reforming Ni(OH)_2 as indicated by the cathodic peak. The discharge current in 15 this 20 mV s^{-1} cycle peaks at 67 mA cm^{-2} and the total charge passed is 257 mC cm^{-2} .

The shape of the voltammogram of Figure 3 more closely resembles that of a battery than a supercapacitor. Here, as is more clearly illustrated in Figure 4, the majority of the charge on discharge is passed above 1.18 V.

20 In order to determine how fast the supercapacitor could be charged and discharged the potential of the device was stepped between 0 V (discharged state) and 1.3 V (charged state) and the current response measured at 25°C. Figure 5 shows a single charge/discharge step sequence. During the anodic spike 800 mC cm^{-2} of charge is passed. Discharge of the device is represented by the large cathodic spike with a maximum amplitude of 50 A cm^{-2} as protons move into the NiOOH . Here,
25 276 mC cm^{-2} is passed during the discharge step, 222 mC cm^{-2} ($7 \times 10^{-5} \text{ C}$ over the 200 μm diameter or 166 mA.h g^{-1}) of which is passed in the first 50 ms.

(vi) Assembly and testing of cycle life of supercapacitor:

In order to examine cycle life, a supercapacitor was assembled in a configuration consisting of mesoporous nickel and palladium electrodes, as prepared in (ii) and (iii)

above, deposited onto 1 cm² evaporated gold substrates, the mesoporous Ni and mesoporous Pd electrodes being separated by a 6 M KOH filled porous PTFE membrane. The cyclability of the nickel-palladium supercapacitor was investigated by continuously cycling the device at 500 mV s⁻¹ in the potential range 0 V to 1.2 V. All 5 performance data are quoted in units with respect to the mass or geometric area of the nickel electrode.

As illustrated in Figure 6, the shape of the voltammogram is considerably different to that presented in Figure 3. The peaks are considerably broader and are separated by approximately 0.5 V as opposed to only 0.07 V in Figure 3. This is due to 10 a combination of the IR limitation imposed on the cell with the introduction of the porous separator and the slow electrochemical response of the Pd, the capacity of which was not significantly larger than that of the Ni(OH)₂ electrode in this configuration. Figure 6 compares the first full 4.8 s cycle with the 15000th. The similar form of voltammogram shows that the electrode has not deteriorated significantly during 15 cycling. A shift in peak potentials towards lower values is believed to be due to oxygen ingress, decreasing the average hydrogen content of the palladium electrode and therefore increasing the potential of the negative electrode. An increase in the charge per cycle is believed to be due to thickening of the oxide layer during cycling.

This result has two implications. The first is that the mesoporous electrodes 20 seem to resist the decrepitation on cycling that is associated with capacity decay in other supercapacitor and battery systems that utilize insertion processes. Thus, a uniform monolithic structure such as that illustrated in Figure 7 appears to withstand the strain of volume expansion and contraction better than those consisting of an aggregation of sintered particles of non-uniform size distribution.

The second implication addresses the fact that not only does the mesoporous Ni 25 electrode capacity resist decay, but actually increases with cycling. This effect is rationalized by understanding that in 6 M KOH under potential cycling conditions the amount of Ni(OH)₂ in a Ni electrode can increase with time as more of the Ni base metal is oxidized. In effect this increases the amount of active material in the electrode 30 and hence the capacity. A number of groups have previously shown that the capacity of an electrodeposited Ni electrode may be increased by up to 30 times by application of

the appropriate cycling conditions in alkaline solution. Here, such a large increase in capacity is not expected in the present arrangement, since during initial cycling already 45 % by mass of the electrode material is utilised. In any case, a large increase in capacity corresponding to complete conversion of the Ni base metal to the electrically 5 non-conducting Ni(OH)₂ would be undesirable since this would destroy the continuous path of Ni metal in the mesoporous electrode which provides electrocal conductivity and acts as a nanoscale current collector (see Figure 7).

EXAMPLE 10

Preparation of a nanostructured nickel hydroxide/carbon supercapacitor.

10 (i) **Preparation of nickel substrate:**

Nickel foil (10 µm thick) was obtained from Johnson Matthey and was prepared as follows, for subsequent deposition of mesoporous nickel.

15 The nickel foil electrodes (4 cm²) were cleaned in an ultrasonic bath of isopropanol for 15 minutes prior to deposition, and were then rinsed with de-ionized water and dried under ambient conditions.

(ii) **Electrodeposition of nickel from an hexagonal liquid crystalline phase:**

A mixture having normal topology hexagonal (H₁) phase was prepared from 45 wt% of an aqueous solution of 0.2 M nickel (II) acetate, 0.5 M sodium acetate and 0.2 M boric acid, and 55 wt% of Brij 56 (Brij is a trade mark) nonionic surfactant 20 (C₁₆EO_n wherein n~10, from Aldrich) Electrodeposition onto the nickel foil substrate was carried out potentiostatically at -0.9 V vs. a saturated calomel electrode and at 25°C using a platinum gauze counterelectrode, according to the method disclosed by Nelson *et al.*, Chem. Mater., 2002, 14, 524-529. After deposition, the films were washed in copious amounts of isopropanol for 24 hours to remove the surfactant. A mesoporous 25 nickel film of approximately 1 micrometer thickness was obtained.

(iii) **Fabrication of a high surface area carbon electrode**

High surface area carbon electrodes were made by mixing 90 wt.% *Norit Ultra* carbon ($1200 \text{ m}^2 \text{ g}^{-1}$), 5 wt. % polytetrafluoroethylene (PTFE), 2.5 wt. % acetylene black (100% compressed) and 2.5 wt. % *Superior* graphite with a pestle and mortar.

5 The paste was then manually rolled into a sheet using a Durston Mini Mill rolling mill (film thickness 50-65 μm). A layer of gold (0.5 mg cm^{-2} , approximately 100 nm thick) was then evaporated onto the carbon films to improve conductivity of the films. The high surface area carbon electrodes had a capacity of $70\text{-}100 \text{ F g}^{-1}$ and a mass of 0.45 mg cm^{-2} .

10 (iv) **Actuation of the Ni and carbon electrodes:**

Cyclic voltammetry experiments were carried out using a Solartron 1287 Electrochemical interface and Corrware software and potential step experiments were done using a custom made potentiostat and ramp generator interfaced with a National Instruments data acquisition card and LabVIEW software.

15 In order to compare the electrochemical characteristics of mesoporous Ni and high surface area carbon, cyclic voltammograms of both types of electrode in 6 M KOH are shown in Figures 8 and 9 respectively. The anodic peak for Ni at 0.46 V vs. Hg/HgO shows oxidation of Ni(OH)_2 to NiOOH via Reaction (1) with subsequent reduction back to Ni(OH)_2 represented by the cathodic peak at 0.32 V. The presence of 20 Ni(OH)₂ is assumed to be due to oxidation of the underlying nickel during preparation, storage and subsequent cycling or conditioning. The latter peak represents the proton storage capacity of the electrode, that is, the reversible capacity of the electrode for proton storage. In Figure 9, this is 104 mC cm^{-2} at 20 mV s^{-1} between 0.6 V and -0.5 V vs. Hg/HgO.

25 The electrochemistry of the high surface carbon electrode in 6 M KOH is typical of pure double layer behaviour and does not exhibit any faradaic electrochemistry. The useful potential window of the carbon electrode in 6 M KOH is only limited by the decomposition of the solvent with hydrogen evolution at the negative limit and oxygen evolution at the positive limit. Based on comparison of the voltammetry of mesoporous

Ni and high surface area carbon, it may be expected that a charge storage device using these 2 electrodes would have a discharge voltage of approximately 1.4 V since this is approximately the potential difference between the onset of hydrogen evolution at the carbon electrode (-1.0 V vs. Hg/HgO) and the intercalation of H⁺ into NiOOH (0.4 V vs. Hg/HgO).

5

(v) Assembly and testing of charge/discharge characteristics of supercapacitor:

In order to study the performance and limitations of mesoporous nickel in a supercapacitor configuration, a negative electrode with higher capacity and power capability was needed. For this purpose, a high surface area carbon film, as prepared in 10 (iii) above, was used. The charge storage capability of the high surface area carbon electrode was made significantly larger than the mesoporous nickel electrode such that performance limitations would be due to limitations in the nickel electrode.

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Accordingly, a two-electrode supercapacitor with a separator (*Celgard*, polypropylene, 25 µm, 2.75 mg cm⁻²) was assembled using a double sided 4 cm² (8 cm² active area) mesoporous nickel positive electrode (prepared as in (ii) above) with approximately 12 µm thickness (including 10 µm thickness of foil current collector) in conjunction with two 4 cm² high surface area carbon electrodes (prepared as in (iii) above) on either side of the nickel electrode separated in each case by a 25 µm *Celgard* separator in 6 M KOH solution. The deposition charge in synthesis of the mesoporous nickel in this case, as prepared in (ii) above, was -3.9 C cm⁻², which corresponds to a mass of 39.4 mg for the nickel sample including the foil substrate and when taking into account a deposition efficiency of 50 %. The total mass of the two carbon electrodes was 28.5 mg and the separators was 25.8 mg, therefore the total mass of the dry capacitor was 93.7 mg.

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The potential of the newly prepared supercapacitor was cycled in the 2 electrode set-up between 0 V and 1.5 V at 5 mV s⁻¹ until the voltammetric response of the capacitor was stable, at this point the charge storage capacities of the carbon and nickel electrodes were considered to be in balance. It was not necessary to charge the positive and negative electrodes separately. Figure 10 shows the cyclic voltammogram of the two-electrode supercapacitor cycled in the potential range 0 V to 1.5 V after it had

become stable. At approximately 1.35 V the device is charged, corresponding to the removal of protons from the $\text{Ni}(\text{OH})_2$ and formation of NiOOH . Discharge occurs as protons move into the NiOOH structure reforming $\text{Ni}(\text{OH})_2$ as indicated by the cathodic peak. The discharge current in this 5 mV s^{-1} cycle peaks at 1.3 mA cm^{-2} and the total reduction charge passed is 133 mC cm^{-2} .

The shape of the voltammogram of Figure 10 more closely resembles that of a battery than a supercapacitor. Here, as is more clearly illustrated in Figure 11, the majority of the charge on discharge is passed above 0.9 V vs. Hg/HgO .

In order to determine how fast the supercapacitor could be charged and discharged the potential of the device was stepped between 0 V (discharged state) and 1.4 V (charged state) and the current response measured at 25°C . Figure 12 shows a single charge/discharge step sequence. During the anodic spike, 105 mC cm^{-2} of charge is passed in 3 seconds. Discharge of the device is represented by the large cathodic spike as protons move into the NiOOH . Here, 95 mC cm^{-2} is passed during the discharge step, 51 mC cm^{-2} of which is passed in the first 100 ms.

EXAMPLE 11

Preparation of a nanostructured nickel / iron supercapacitor.

(i) Preparation of nickel substrates:

For the mesoporous nickel films, nickel foil ($10 \mu\text{m}$ thick, 4 cm^2) was obtained from Johnson Matthey and was prepared as follows, for subsequent deposition of mesoporous nickel.

For the iron films, nickel foil (Goodfellow, $10 \mu\text{m}$, 2 cm^2) was prepared as follows for the subsequent deposition of mesoporous iron.

The nickel foil substrates were cleaned in an ultrasound bath of isopropanol for 15 minutes prior to deposition, and then rinsed in de-ionised water and dried under ambient conditions.

(ii) Electrodeposition of nickel from an hexagonal liquid crystalline phase:

A mixture having normal topology hexagonal (H_I) phase was prepared from 45 wt% of an aqueous solution of 0.2 M nickel (II) acetate, 0.5 M sodium acetate and 0.2 M boric acid, and 55 wt% of Brij 56 (Brij is a trade mark) nonionic surfactant (C₁₆EO_n wherein n~10, from Aldrich). Electrodeposition onto the nickel foil substrate was carried out potentiostatically at -0.9 V vs. a saturated calomel electrode and at 25°C using a platinum gauze counterelectrode, according to the method disclosed by Nelson *et al.*, Chem. Mater., 2002, 14, 524-529. The total deposition charge was 2.0 C. After deposition, the films were washed in copious amounts of isopropanol for 24 hrs to remove the surfactant.

(iii) Electrodeposition of iron from a hexagonal liquid crystalline phase:

A mixture having normal topology hexagonal (H_I) phase was prepared from a deoxygenated, 40 wt.% of aqueous solution of 0.2 M iron (II) sulphate and 60 wt.% Brij 56 nonionic surfactant (C₁₆EO_n wherein n~10, Aldrich). Electrodeposition onto a nickel foil substrate (2 cm² in area) was carried out potentiostatically at -0.9 V vs. a saturated calomel electrode and at 25 °C using a platinum gauze counterelectrode. After passing 0.2 mAh of charge, the film was removed from the deposition mixture under cathodic protection by attaching the films to zinc foil immediately prior to the films being isolated from the deposition potential. The film, together with the zinc foil, was washed in copious amounts of deoxygenated acetone for 1 hour to remove the surfactant.

(iv) Examination of the iron electrode:

After washing, the iron electrode was immersed in 6 M aqueous KOH and the zinc was disconnected. The open circuit potential was measured and found to be 1.1V versus a charged nanostructured NiOOH electrode. Cyclic voltammetry experiments were carried out using a Solartron 1287 Electrochemical interface and Corrware software.

A cyclic voltammogram of the iron electrode in 6 M KOH was performed at 20 mV s⁻¹ and the result is shown in Figure 13. This shows an anodic peak at -1.0 V vs. Hg/HgO and a cathodic peak at -1.1 V. The total charge passed between -1.0 V and -

0.3 V in the anodic peak was 17 mC. The cathodic charge passed between -0.3 V and the interference of hydrogen evolution at -1.15V was 25 mC as shown in Figure 14.

(v) Assembly and testing of charge/discharge characteristics of the supercapacitor:

5 The iron and nickel electrodes prepared as described above were immersed into a 6M solution of KOH. The open circuit potential was measured and found to be 1.1 V. The two electrodes and the solution thus constituted our capacitor for cycling tests.

The potential of the newly prepared capacitor was cycled between 0 V and 1.4 V at 5 mV s⁻¹. Figure 15 shows the cyclic voltammogram of the two-electrode
10 supercapacitor. The discharge, plotted as a negative current, shows a broad peak around 1.1 V with a peak current of 0.15 mA. The total charge stored was found by integration of the voltammogram in Figure 16 to be 12 mC.